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MORPHOLOGY CONTROL OF PHOTOELECTROCHEMICALLY ETCHED PROFILES IN n-GaAs

by

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Photoelectrochemical etching of (100) n-GaAs along the $[01\bar{1}]$ crystallographic direction produces V-grooves. It was determined that the groove angle and rate of undercutting of the photoresist mask was dependent on electrolyte composition, light intensity and bias potential. Grating structures could be produced in neutral aqueous electrolytes containing KCL, with angles varying from 80 to 120° as the KCL concentration was varied from 0.01M to 4M. The angles could also be controlled with applied bias and with light intensity. The V-grooves are formed due to the exposure of Ga-rich faces, their composition and angle probably depending on the extent of adsorption of Cl^-. Non-adsorbing electrolytes such as F^- and SO_4^- generally gave rougher morphologies and/or passivation.

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Morphology Control of Photoelectrochemically Etched Profiles in n-GaAs

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Photoelectrochemical etching has recently been employed as a means for fabricating microstructures such as diffraction gratings in III-V semiconductor materials. Of particular significance is the dependence of etching profiles on crystallographic orientation. Work in this laboratory has shown that V-grooves could be produced by photoanodic etching in GaAs using a periodic mask to define the spacing [1-3]. Key to the process for producing symmetrical grooves is the alignment of the pattern on the (100) surface along the [01$\bar{1}$] direction. The actual V-groove profiles have been assumed to arise from the exposure of (111)Ga planes. However, it became obvious during the course of our work that the groove angles and morphology had a dependence on electrolyte composition and other process parameters such as light intensity. Reported here are the results of investigations into the effects of supporting electrolyte, light intensity, doping density, applied potential and photoresist processing on the photoelectrochemically etched V-groove structures in n-GaAs.

The photoelectrochemical etching experiments were carried out on single crystal (100) GaAs substrates obtained from MA/COM Laser Diode Inc. and Bertram Laboratories. The crystals were Si-doped, n-type with carrier densities of 5×10^{17} and 6×10^{18} cm^{-3}. A stripe photoresist mask with periodicity of 50 lines/mm with a line/space ratio of 2 and was applied to the (100) surface and aligned along the [01$\bar{1}$] direction. The thickness of the mask determined with a Sloan Dektak profilimeter was 1.5 ± 0.2 μm.

Photoelectrochemical etching was carried out in a 3-electrode configuration using an SCE reference electrode, as described previously [2]. Irradiation was conducted using an Oriel 500W Hg(Xe) photoresist exposure illuminator with a ±5% beam uniformity over a 20 cm^2 area. The filtering was such that the irradiation wavelength was distributed between 350-450 nm. Most experiments were conducted at an intensity of 30 mW/cm^2. In some experiments, the light was focused onto the electrode surface using a convex lens and adjusted to an intensity of 300 mW/cm^2.

The transmittance spectrum of the 1.5μ thick photoresist film was recorded on a quartz substrate and found to be >60% transmissive between 300 and 900 nm, where GaAs absorbs. During the photoetching, therefore, the GaAs covered with 1.5 μm photoresist film is illuminated as well as the surface not covered by the mask. This process of delivering light beneath the mask is responsible for undercutting the photoresist and eventual formation of the connected V-grooves.

As summarized in Table 1, V-grooves etched under the conditions described had interior angles that increased with increasing KCl concentration. In addition, as the concentration of KCl was increased, the walls of the etched grooves became noticeably rougher, taking on a distinctive scalloped morphology. For comparison, photoelectrochemical etching of V-grooves was done in neutral aqueous solutions using Na_2SO_4 and NaF as supporting electrolytes. In 0.5M KCl or Na_2SO_4, the limiting photocurrent was proportional to the light intensity up to the highest intensity used (300 mW/cm^2) and remained steady with time. In 1M NaF at 30mW/cm^2, the photocurrent decreased by nearly 80% over the same time period, indicating passivation was taking place at the GaAs surface. Both the shape and the surface texture of the V-grooves were affected by the composition of the electrolyte. A very shallow V-groove pattern with neither sharp peaks nor flat bottoms was formed in the 1M NaF electrolyte. In addition, some precipitation of particles was observed at the bottom of the grooves in support of the surface passivation suggested by the photocurrent decay. The V-groove etched in Na_2SO_4 had a rough interior wall, and the bottom of the groove did not reach a point. Thus, only the lower concentration KCl solutions gave rise to smooth walls.

Table 1

Effect of KCl concentration on the angle of photoelectrochemically etched V-grooves in n-GaAs.

Category	[KCl] Ml^{-1}	Interior Angle (degree)	Crystal Faces
I	0.05 - 0.2	70 - 85	(111)Ga, (332)Ga
II	0.2 - 1.0	90 - 100	(223)Ga, (335)Ga
III	1.0 - 3.0	105 - 115	(112)Ga
IV	>3.0	120 - 130	(113)Ga

It is likely from these results that Cl^- participates in the electrodissolution of Ga surface sites via specific adsorption. Such a mechanism has been suggested by Kohl et al. during the photoanodic dissolution of n-InP and n-GaAs in aqueous HCl and HBr [4]. A simplistic yet useful model of the (111)Ga surface is that Ga atoms are bonded to three As atoms below the surface, and an empty sp3 hybrid orbital is available for complexation. Gerischer [5] proposed that the photodissolution of a III-V semiconductor is initiated by nucleophilic attack by an anion with a photogenerated hole:

$$GaAs + Cl^- + h^+ \rightarrow\ \ >Ga - Cl + As<$$

Of the anions investigated, Cl^-, F and SO_4^{2-}, Cl^- is absorbed most strongly onto Ga metal electrodes [6]. Since the fluoride anion is nonpolarizable, it only forms solution complexes and does not participate as a photodissolution intermediate. A higher dissolution rate, therefore, can be expected with an increase in Cl^- concentration. If the Ga dissolution rate is enhanced to such a degree that it becomes comparable to the As dissolution rate, the etching of GaAs will become isotropic. For example, Shaw [7] reported that (111)Ga plane is revealed on chemical etching of GaAs with 0.27M HCl, 0.87M H_2O_2, but the etching becomes completely isotropic, with rounded profiles, in 10.6M HCl, 0.87M H_2O_2. The V-grooves formed by anisotropic etching result from the reactivity differences of the surface atoms and can be produced at (100) faces only along the [01$\bar{1}$] direction. The (hhk)Ga faces and approximate interior angles are as follows: (111)-70°, (332)-80°, (223)-90°, (335)-95°, (112)110°, (113)130°, and (114)-142°. The faces that are observed appear to represent free energy minima for any given set of conditions. Significantly, a (332)Ga plane is revealed at intermediate acid concentrations in the work of Shaw [7]. These surfaces may be constructed from regular progressions of steps added to fundamental (111)Ga face [8]. Similarly, scalloped sidewalls are observed in grooves etched at high Br_2 (MeOH) concentrations, indicating the stability of high order crystalline habits [9].

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